UNITED STATES PATENT OFFICE.

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ART OF TREATING FIBROUS MATERIAL.

No. 831,621. Specification of Letters Patent. Patented Sept. 25, 1906.

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To all whom it may concern:

Be it known that I, BENJAMIN C. MUDGE, a citizen of the United States, residing in Boston, in the county of Suffolk and State of Massachusetts, have invented certain new and useful Improvements in the Art of Treating Fibrous Materials, of which the following is a specification.

My invention relates to the manufacture of flax, linen, or other fibers, and especially to the production of linen fiber of superior quality for use in the mechanical arts.

More especially, my invention pertains to the transformation or removal, or both, from flax fiber of those portions of the flax-plant or stalk known in the art as "shives," "boon," or "sprits," and is in part in the nature of an improvement upon the subject-matter disclosed and claimed in United States Patent No. 732,103, granted to me June 30, 1903.

My improved process is also applicable both to manufactured or partially manufactured flax or linen products.

I have found that the fiber constituting the shive part of the flax-straw is substantially of the same nature as the fiber constituting the long line fiber or linen of the plant and that when reduced to its ultimate or net fibrous condition these shive fibers may become a part of the flax or linen fiber of commerce and be useful in like manner.

My present improvement is applicable, as is my before-mentioned invention, to the treatment of flax generally, including the flax waste or ordinary flax tow of commerce. Usually and preferably the flax is first subjected to a preliminary or partial deshiving, which may be accomplished by well-known mechanical means with efficiency and economy. In this preliminary deshiving I preferably use some well-known means—such, for instance, as an ordinary duster mechanism—and a modified woolen-garnet machine. The fiber is thus cleaned of refuse and loose foreign matter and a quantity of the shives are mechanically removed from the fiber. The state of the fiber after being thus treated is partially deshived and is in a general way commercially called "deshived." Under the general term "shive" I include all such parts of the flax-plant as are of a woody or straw-like nature, this referring especially to the plant stalks and stalk units. The flax is next subjected to the operation of degumming. This consists in a partial dissociation and partial removal of the gum, lignin, pectose, fatty acids, and wax-like substances. For this treatment the bath is alkaline and may be composed of any suitable alkali, but I preferably employ the same ingredients, to wit, soda-ash and caustic soda, as used in my already patented improvement; but I have found that substantially equal parts of these materials have a better and also a more efficient action than those stated in my before-mentioned patent. This bath I preferably use at about 3° Twaddell and at a temperature of about the boiling-point or upward. This temperature (if above boiling) I obtain, preferably, by steam heat in a digester, and I preferably use a digester which can be agitated or rotated, as I find that the agitation of the material operated upon with respect to its container, or vice versa, tends to hasten and render more effective this operation. This also applies, generally speaking, to the other chemical operations and rinsings involved in practicing my improved process. The said agitation tends to hasten these various operations by affording the liquors of said baths respectively a larger opportunity for contact with the material subjected to their action by washing away from contact with the fiber such portions of the liquor as are more or less spent, and to thereby tend to facilitate the supply of liquor of maximum strength to the various parts of the material treated and also to mechanically remove portions of the matter acted upon. In the foregoing bath substantially equal proportions of soda-ash and caustic soda are used, for the reason that I believe said chemicals when so used produce a materially less harsh action on the fiber and are under better control. It is also feasible and I have with a large measure of success used in this bath either of these ingredients to the exclusion of the other by sufficiently increasing the quantity of the one to compensate for the absence of the other or to compensate for variations in time or temperature; but, as above stated, I deem substantially equal proportions especially advantageous as regards chemical action and also as to economy in cost as compared with the work accomplished. After the flax has remained a sufficient time in this bath I

draw off the liquor or remove the flax therefrom and then preferably rinse with water.

The next stage of the treatment is souring. For this I subject the flax to the action of slightly-acidulated water, preferably by immersing the flax therein, and I have found that three-quarters of an hour is usually a sufficient time in which to accomplish the desired result. I then submit the flax to hypochloritic action, which results in indirect oxidation of the extraneous organic and inorganic non-fibrous matter by the union of its hydrogen with the chlorin, thereby liberating the oxygen of said extraneous matter, which thereupon performs its well-known bleaching action. Coincident and coöperative with this action is the continued disintegration of the shive masses through the union of the chlorin with their lignin and other cementitious matter, thereby forming a soluble chlorid of lignin and other chlorids which are disseminated through the bath. This hypochloritic bath may be prepared with various ingredients and by various methods; but I have found the following ingredients and method to be economical and efficient. I dissolve six and one-half parts of chlorid of lime, one part of soda-ash, one part of caustic soda, and one and one-tenth parts of sulfate of magnesia in a sufficient quantity of water, preferably at about 90° Fahrenheit, to show about 3½° Twaddell. The specified proportions of these ingredients are approximate. I preferably use only the clear liquor resulting from this mixture and remaining after the settling out and skimming off of impurities and preferably at a temperature of about 120° Fahrenheit.

After the hypochloritic treatment above set forth I treat in acidulated water for a suitable period—for instance, about one-half hour—with the objects in view, among others, of further dissolving such compounds as may have been formed by the prior treatment, the further direct action upon the gums and cements constituent in the mass more readily susceptible to the action of acids, and to put the material into better condition to properly receive the subsequent chemical treatment. For this acid treatment I usually and preferably employ as a suitable acid about one-eighth per cent. of sulfuric acid. The acid employed and its strength, as well as its temperature and the duration of its action, must vary and depend upon each other to some extent and upon the natural features of the plant or flax being treated. In this connection I have found that other acids—such as chlorhydric, nitric, acetic, oxalic, and others—give good results, and some of these being milder in their action are sometimes preferable where it is desired to treat the fiber with great care and conserve all its natural features for the production of a fine fiber. For these reasons such acids may be used as alternatives and of a strength in proportion. It is to be noted in this connection that geographical location, soil, and climatic conditions have substantial effects upon the growth and quality, coarseness or otherwise, of the plant fiber and the proportions of cementitious constituents or matrix to the volume of the fiber of the plant. Also there is a marked difference in the readiness with which the shive portions of these various plants may be broken and removed by mechanical means, and consequently in the relative quantity of shives remaining to be treated by chemical action.

Before treating in acidulated water, as last stated, I may rinse, by agitating in water or otherwise, the mass under treatment, and under some circumstances this is deemed desirable. I have found, however, that generally and in what I deem the best practice the carrying over of a part of the hypochlorites associated with the fiber into the acid-bath is beneficial, and I therefore generally prefer to omit this washing. Among these benefits are a better control of the operations of the process through the balancing of the action of one chemical against another, and by reason of the already close association of the hypochlorites with the flax fiber the acid-bath evolves a chlorin gas in immediate contact with the flax fiber, showing the bleaching thereof and the relative condition and progress of the operations of the process. After this acid treatment I rinse the flax in water. This and the degree of the rinsing will depend upon the exact nature of the chemicals employed and of the antichlor to follow. Resulting from previous chemical action undesirable by-products and insoluble salts have resulted, such as sulfate of lime and sulfate of calcium, which exist as deposits on the fiber. If not removed, these deter progress and obstruct the action of the antichlor. Also in the subsequent use of certain antichlors some acid would coöperate and be beneficial, and in such case it need not be removed by rinsing. Respecting this rinsing, therefore, and the selection of the subsequent antichlor, judgment should be used. Either the acid must be washed out or an antichlor employed to which acid is no objection, or the non-soluble deposits must be removed before employing an antichlor to which they are obstructive.

Following the acid treatment I then stop the further action of any remaining chlorin by submitting the mass under treatment to the action of an antichlor, preferably acid sulfite of calcium in an aqueous solution. I give preference to acid sulfite of calcium, as I have discovered that it possesses superior antichlor properties and on account of the bleaching properties of said acid sulfite and also because it unites with and dissolves the lignin, thereby continuing the disintegration

of the shive mass and the dispersion of its fibers. I preferably subject the flax to the action of this bath for about one-half hour. My second choice of an antichlor is bisulfid of soda, which I have discovered to have effective antichlor properties. This agent I do not consider quite the equal as an antichlor to the acid sulfid of calcium, but analogous thereto, and which assists in some degree toward the disintegration of the shives and the bleaching thereof. I find in practice that in combination with either of the above-mentioned antichlors the addition of an acid tends to augment and accelerate the operation of the antichlor and the results mentioned. It is known that hyposulfite of soda is an antichlor and it may be used instead of either of the foregoing compounds in this bath, but it has little or no effect in assisting the disintegration of the shives or in bleaching. This material is, however, of low cost, and therefore may be used with economy locally, because of its efficiency as an antichlor only. An objection to the use of hyposulfite of soda is that a deposition of flowers of sulfur adhering to the fiber in an amorphous sticky condition may result from its contact with certain acids, such as sulfuric acid, impairing the process and diminishing the quality and value of the product. I have also discovered that acid sulfid of calcium, bisulfite of soda, and hyposulfite of soda may be used together, mixed in varying proportions as an antichlor, disintegrator, and bleacher of shives. An advantage of this mixture is an economic one, hyposulfite of soda being possibly the cheapest and most common, and its efficiency can be increased more than proportionate to the additional cost by the addition of either one or both of the other two.

After the antichlor treatment we now have a mass of fiber remaining partially incased in its organic gums and vegetable-matrix combined with a remnant of coloring-matter, and all of which substances so associated with the fiber have been influenced and modified by previous treatment, whereby they are made susceptible to further treatment by different or other and gentler means. A substantially further continuance of the means heretofore used has been found injurious to the fiber now less protected by its organic gums than previously, whereas said gums have now been rendered susceptible to treatment by means not previously effective. The mass composed as last treated by me will have entrained therein a remnant of the antichlor with the by-products resulting from its action, and it is therefore important to remove mechanically by washing, rinsing, or draining these now foreign substances. The carrying over of these substances will both impede and tend to counteract the action of the subsequent chemical treatment. I then submit this fibrous mass consisting of partially-bleached flax fiber and partially-disintegrated and partially-bleached shives to a further and direct oxidation. The object of this treatment is to complete the disintegration of the shive portion of the mass and, incidentally, to remove any remaining coloring-matter, whether organic or stains, from foreign sources. The office of this solution is to provide oxygen in a form to readily combine upon contact with the gums and other non-fibrous components.

It has been stated that the fibrous portions have been partly freed from their organic gums and other incasing substances and that they are now, therefore, more exposed to injury by harsh treatment, whereas the gums and other associated substances require further treatment for their complete removal. The chief characteristic of the process heretofore has been the alternate treatment by alkaline and acid solutions. It is now necessary to keep the dividing-line between these two conditions a narrow one and under ready and quick control. The oxidizing solution should be kept always on the acid side. If not, it will result in the speedy destruction of the fiber, for the reason that in a non-acid, neutral, or alkaline solution the oxidizing agents will at once attack the cellulosic tissues and convert them into oxycellulose. This destructive action carried even to a small extent would materially injure the fiber by weakening it, and thus reduce its value. The base of this oxidizing solution is an acidulated water, in which the oxidizing ingredients are dissolved in desired proportions. As oxidizing ingredients I preferably employ permanganate of potash, in combination with chlorate of potash in proportions to suit the purpose. The advantage of employing both is that the chlorate assists and makes more active the oxidizing effect of the permanganate of potash, and is therefore a factor in the control and in the intensity of the action. The dominant factor as an oxidizing agent is the permanganate of potash. This may be used alone or in combination with other things, and I have found it to be highly active and advantageous, and because of the ready and exact control to which it lends itself in combination with other oxidizing agents or assistants I consider it to be a factor of substantial value in this connection. As an alternative assistant to the permanganate of potash I have found valuable results from the use of sulfate of magnesia instead of the chlorate of potash; but if used its proportion to that of the permanganate should preferably be substantially equal. There are doubtless other alternative assistants. There are also other oxidizing agents which may be used alone, and I have found that a bath of manganate of soda may be substituted for permanganate of potash, but with

less beneficial results. In some localities, however, the low cost of manganate of soda may make its use relatively economical. In using permanganate and chlorate of potash I preferably used them in proportions of about eight of the former to one of the latter and dissolve these ingredients in an acidulated water. This acidulation is very slight, but should be acid in fact and enough to counteract the influence of any alkali and to prevent the oxygen attacking the fiber. The exact or extreme degree of the acidulation may therefore vary and if excessive may be corrected by the addition of further alkali. The strength of the bath in oxidizing ingredients is preferably less than 1° Twaddell. Incidental to the application of this bath the fibrous mass assumes a reddish-brown color, indicating the proper action of the bath and its progressive degree in the formation of peroxid of manganese. Upon attaining this color, which is usually assumed in substantially less than one hour's time, depending upon the mechanical means employed to apply the liquor and the strength of the ingredients and the temperature, it is ready for another rinsing.

The previous operations have resolved the bulk of the lignin into chlorid of lignin and the pectose into metapectic acid, the bulk of which have by this time been dissolved in the various baths. The effect of this oxidizing treatment upon the fibrous mass is to complete the dissociation of the shive fibers and to convert the remaining lignin and pectose into soluble compounds and to render finally soluble the remaining gums, the removal of which carry with them any remaining coloring-matter. These conditions are indicated by the degree of the brown color above referred to. I thereupon rinse the fibrous mass with water to assist in removing entrained portions of the solution and to remove such portions of said mass remaining as are soluble in water or removable thereby. I then subject the fibrous mass to a bath, commonly known as a "discharging-bath," which discharges or removes the color imparted by the permanganate bath and any remaining organic coloring-matter and disintegrates any last vestiges of shives and does this while avoiding any injury to the fiber. This bath comprises an acid solution of sulfur, and I preferably use a solution of acid sulfite of calcium in slightly-acidulated water. From this solution is liberated sulfurous-acid gas. I also preferably use this at a high temperature, approximately boiling, thereby facilitating the liberation of the sulfurous-acid gas. I have had good results in using acid sulfite of calcium and sulfuric acid in about the proportion of four of the former to one of the latter. The strength of this bath in acid sulfite of calcium and in the acid used to acidulate the water will be influenced by the temperature and should be sufficient to completely remove the peroxid of manganese indicated by the color mentioned, in doing which the remaining organic coloring-matter will disappear, and if any shive remnants remain they may be disintegrated by increasing the strength of the bath. This discharge bath I follow with a final rinsing in water; otherwise upon coming in contact with alkali upon use or in subsequent manufacture the color may reappear.

It has already been mentioned in the case of the flax-plant that a substantial variation is found in the quality and size of the fiber and its tenacity or resistance to treatment both when considered chemically as to its constituents and mechanically as to their hardness and tenacity. For these reasons these various stages of the process and the several chemical treatments affect the shive portions and cementitious gums differently. It may not be feasible to say at just what stages in the operation the disintegration of the shives and cements takes place, and it is perhaps immaterial to know or to state this definitely. It is known, however, that each successive action tends to weaken the stability of the shive as a unit, and its size and the relative amount of work to be done in its disintegration will somewhat depend upon its size and the mechanical agitation applied to it. As its cementitious bond becomes progressively weaker mechanical agitation will tend further to reduce it. What is of greater importance is the fact that it becomes constantly more susceptible to treatment, and the object of the process and the skill involved in its practice is to apply to the constantly-weakening shive an influence sufficient to disintegrate it and not affect detrimentally the fiber which is being more and more denuded of the coatings which originally protected it. It is also known that each step in the process renders the fibrous mass more susceptible to the influence of the succeeding step. Therefore the intensity of the treatment is progressively decreased to preserve the fiber. It is further known that temperature may be used as a powerful factor. Temperature does two things. It makes more active the properties of the chemicals *per se* and also makes more susceptible to their action or influence the subject-matter under treatment without affecting in the same way the fiber. In the practice of the art, therefore, these conditions should be regulated accordingly. It is also pertinent to note that the factor of time or duration is of importance and wields a powerful influence at all stages of the process and conditions of the mass under treatment, depending upon the particulars of those features, and whereas the actual state of the fiber itself is at no time affected or impaired it is increasingly denuded of protecting-covers; but the

ingredients sought to be removed, as well as the previously-combined elements and the by-products, require time for their interchangeable action on each other, and the relative proportions and strength employed make it necessary to vary their exposure to the influence of each other. In some cases a chemical strength sufficient to quickly influence the extraneous portions of the mass would be injurious to the fiber, and more time must therefore be permitted for this action in lieu of an increase of strength.

I claim—

1. That improvement in the art of treating fibrous plants which consists in subjecting the same properly prepared to the action of an alkali, then to an acid treatment, then to the action of hypochlorite of magnesia, then to an acid treatment, then to the action of an antichlor, then to a peroxid treatment, and then to the action of sulfurous-acid gas, each in successively-decreasing chemical intensity.

2. That improvement in the art of treating flax and analogous fibrous materials which consists in subjecting the same to an aqueous alkaline solution at a temperature above boiling, then to a hypochlorite, then to an antichlor, and then to oxidation and discharge.

3. That improvement in the art of treating flax and analogous fibrous materials which consists in partially degumming and partially deshiving fiber, then subjecting the same to the combined action of the hypochlorites of soda and magnesia, then to an acid treatment, then to the action of acid sulfite of calcium, then to the action of permanganate of potash, and then to the action of sulfurous-acid gas.

4. That improvement in the art of treating flax and analogous fibrous materials which consists in partially degumming and partially deshiving fiber, then subjecting the same to the action of a chlorid, then to the action of an antichlor, then to the action of an oxidizing agent, and then to the action of a discharging agent.

5. That improvement in the art of treating flax and analogous fibrous materials which consists in subjecting the flax, previously suitably prepared, to the following series of treatments in successively-decreasing chemical intensity, the same being applied hot and in the order named: an alkaline treatment; an acid treatment; a hypochloritic treatment, an acid treatment; an antichlor treatment; a water treatment; a peroxid treatment; a sulfurous-acid-gas treatment, and a water treatment.

6. In the decomposing and removal of the organic gums and stalk units of flax, the art which consists in the application of a series of successive and alternate alkaline and acid solutions to the plant mass, followed by an antichlor to check further action of said solutions, and followed by an oxidizing solution and a discharging solution.

7. In the decomposing and removal of the organic gums and stalk units of flax, the art which consists in the application of a series of successive and alternate alkaline and acid solutions of the plant mass, followed by an antichlor to check further actions of said solutions, and followed by a solution of peroxid of manganese and agents to generate a sulfurous-acid gas adjacent to the plant fiber.

Signed at Nos. 9 to 15 Murray street, New York, N. Y., this 12th day of November, 1903.

BENJAMIN C. MUDGE.

Witnesses:
FRED. J. DOLE,
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